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CHAPTER IV --

ELECTROKINETIC PROCESSES

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A. Electroosmosis and Electrophoresis.

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If the liquid comes in contact not with the stationary walls of the diaphragm capillaries, but with mobile particles of some substance, for instance with solid or liquid colloidal particles or with small gas bubbles, a flow of these particles toward one or the other of the electrodes will take place. Such a flow of particles relative to the liquid in contact with them is called electrophoresis.

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The suspended particles undergoing electrophoresis may be solid, liquid or gaseous. Liquids undergoing electroosmosis may be of widely different nature: water, methyl alcohol, acetone, nitrobenzene, pyridine, turpentine, toluol, and the like, Porous partitions (diaphragms) can be made of asbestos, fire clay, parchment, animal charcoal, silk and the like.

Depending upon the nature of the liquid, the material of the diaphragm and other conditions, electroosmosis may take place toward the cathode as well as toward the anode. In a similar manner electrophoresis can take place toward the cathode or the anode depending upon the nature of the particles and the liquid in which the particles are suspended. The direction of the flow is determined, to a considerable extent, by admixtures to the liquid, especially of electrolytes. The effect of the latter can be so pronounced that the direction of the flow can be in reverse direction to that occurring in the pure liquid.

1. Electrokinetic Potential

The cause of electroosmosis and electrophoresis is the potential which arises at the boundary of contact of the phases, and the electric field between the electrodes, formed as a result of potential differences applied to the electrodes.

Magnitude of Potential at Phase Boundary

The boundary separating two phases is always the site of a potential drop. Whether a metallic conductor is in contact with a solution of a salt of the same metal, or whether two

dielectrics are in contact -- both phases in contact with one another are charged with electric charges of opposite signs. Between the phases there arises thus a difference in potential, or a potential drop, and there is formed as a result a double electrical layer. The structure of the double electrical layer may vary. The greater the concentration of the electrolyte and the valency of the ions, the more closely the double electrical layer approximates by its structure that of a plate condenser wherein the opposite charges are located in the immediate vicinity of the partition surface. In solutions having a low concentration of ions, in which strong manifestation of electrophoresis and electroosmosis phenomena takes place, charges within the liquid phase are distributed over a certain thickness of the liquid. The structure of the double electrical layer in such an instance is illustrated diagrammatically in figure 64. Greatest charge density is present near the partition surface, and the density of the charges decreases with increasing distance from that surface. Thus the double electrical layer in weak solutions of electrolytes is of a diffused nature. The total potential drop between phases, that is, difference of potentials between the phases beyond the limits of the diffused electrical layer, is sometimes called the thermodynamic potential and is denoted by the Greek letter ϵ (epsilon).

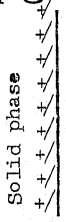

Figure 64. Structure diagram of double diffused electrical layer.

If in the electrokinetic processes the displacement of the liquid in the course of its motion did take place precisely at the surface of partition of the phases, then the difference of potentials between the moving layers of the liquid and the stationary phase, or between the mobile colloidal particle and the stationary liquid, would be equal to the total thermodynamic potential ϵ.

But this does not take place. A portion of the liquid layers always remains stationary in contact with the surface of the other phase. Displacement of the liquid layers takes place at a certain distance from the partition surface, that is, within the diffused electrical layer. The potential drop between the stationary and the mobile phase is thus less than ϵ and is equal to the difference of potentials between the stationarily bound and the moving layer of liquid. This potential drop is called the electrokinetic potential and is denoted by the letter ζ (zeta) to differentiate it from the total thermodynamic potential ϵ.

Correlation between the thermodynamic potential ϵ and the electrokinetic potential ζ is shown graphically in figure 65. The curve a b represents the decrease of potential within the diffused layer d. The ordinate ϵ corresponds to the total drop of potential ϵ. On motion of the liquid with respect to the phase D displacement takes place along the line A B. The liquid layer $\triangle$ is stationarily bound to the surface of phase D. The Electrokinetic potential ζ corresponds to the ordinate ζ. It is, as is apparent from figure 65, smaller than the thermodynamic potential ϵ, by the value of the decrease of potential within the stationarily bound layer of liquid.

Figure 65. Potential at phase boundary.

The thickness of the diffused layer has an effect upon the value of the electrokinetic potential, which decreases with decreasing thickness of the layer. In that instance where, due to the action of some factors, the thickness of the diffused layer is decreased to that of the stationary adsorbed layer of liquid $\triangle$, the thickness of which is approximately of molecular dimensions, and the double electrical layer acquires the structure of a plate condenser, the electrokinetic potential becomes equal to zero while the value of the thermodynamic drop of potential remains unchanged.

Sign of Potential and Direction of Electroosmosis and Electrophoresis

The motion of liquid on electroosmosis and that of the particles on electrophoresis depending upon the sign of the electrokinetic potential takes place toward one or the other electrode. The sign of the electrokinetic potential of the liquid, or particle, depends upon the nature of the phases in contact and the admixtures of the liquid (especially of electrolytes). For example, glass on contact with water acquires a negative charge, while on contact with turpentine -- a positive charge; a diaphragm made of filter paper on contact with benzene, becomes charged negatively, and the benzene is charged positively; the same diaphragm on contact with chloroform becomes charged positively and the chloroform negatively.

A general guiding indication for the determination of charge sign of a phase is given by the rule: On contact of two dielectrics a positive charge is acquired by the substance having a higher dielectric constant. Thus water having a high dielectric constant (D = 81), on contact with various substances in most instances becomes charged positively, and consequently on electroosmosis it flows toward the cathode. This rule, however, is applicable only to pure liquids, and loses completely its significance in the presence of electrolytes. But even in the case of pure liquids, there are exceptions. Thus bubbles of air ($D \approx 1$) suspended in water, move in accordance with the indicated rule, toward the anode, but suspended in benzene ($D \approx 2$) and in introbenzene ($D = 35 \div 38$) they move toward the cathode.

Influence of Admixtures upon Magnitude and Sign of the Electrokinetic Potential

The magnitude and sign of the electrokinetic potential, and hence the direction of electroosmosis and electrophoresis, are influenced to a considerable extent by the presence of surface-active substances, polyatomic alcohols, soaps, alkaloids and especially of electrolytes. The effect of electrolytes can be so pronounced that not only a decrease of the charge takes place but sometimes also a change of its sign. This constitutes the substantial difference between thermodynamic and electrokinetic potentials. The former is but little altered by the presence of acids and salts, which do not contain the same ions as the electrode; the latter is changed the more strongly, the greater the valency of the ion and its adsorbability. Electrolytes present in minute amounts,

measured in millionth parts of a mole, already have an effect on the electrokinetic potential. The effect of electrolytes upon the electrokinetic potential can be formulated in the following manner: The greater the valency of the cation of an added electrolyte, the more pronounced is the decrease of the negative potential and on the other hand, the greater the valency of the anion, the more pronounced is the decrease of the positive potential. All the characteristic properties of the electrokinetic potential, and in particular the effect upon it of minute admixtures of electrolytes are explained by the structure of the double diffused layer and adsorption phenomena, a detailed discussion of which is the subject matter of specific disciplines.

2. Velocity of Electroosmosis and Electrophoresis

Experimental study of electroosmosis and electrophoresis shows that velocity of liquid motion with respect to stationary walls of the capillary, and that of the suspended particles with respect to the liquid, depend on the magnitude of electrokinetic potential, the potential gradient (that is, difference of voltage applied to the electrodes, per one centimeter of the path) the dielectric constant of the liquid and the internal friction of the liquid.

Mathematically the velocity of liquid motion is expressed by the equation:

$$w = \frac{\zeta h D}{4\pi \eta} \qquad (1)$$

where W is the velocity of liquid motion with respect to the stationary wall in centimeters per second.

ζ - the electrokinetic potential in volts

h - the potential gradient in volts per centimeter

D - the dielectric constant

η_l - viscosity of the liquid in poises.

For practical computations, however, it is more convenient to calculate not the linear velocity of liquid motion, but its volumetric velocity as a function of current intensity passing through the apparatus, and of the specific electrical conductivity of the liquid. This dependence is expressed by the equation:

$$v = \frac{\zeta I D}{4\pi \eta_l M} \qquad (2)$$

where V is the volumetric velocity of liquid flow through the diaphragm, in cubic centimeters per second.

ζ - the electrokinetic potential

I - current intensity

M - specific electrical conductivity of the liquid.

From equation (2) we can deduce a very important practical conclusion, namely, that the volumetric velocity of liquid flow through the diaphragm depends, all other conditions being equal, only on the intensity of the current passing through the apparatus, and does not depend on either the area of the diaphragm or its thickness. From equation (2) it is also apparent that insofar as effectiveness in practice is concerned, only those liquids can be subjected to electroosmosis which have a very low electrical conductivity.

Velocity of motion of a suspended particle can also be expressed by means of equation (1). However, equation (1) gives the velocity of particles having a cylindrical shape. For particles having the spheric shape, there is applicable an equation having a different numerical coefficient. In such an instance the velocity is expressed by the equation:

$$w = \frac{\mathcal{E}\, h\, D}{6\pi\eta} \qquad (3)$$

Equations giving the electrophoresis velocity also permit reaching an important practical conclusion, namely: the velocity of suspended particles motion is independent from their size.

3. Technical Application of Electroosmosis and Electrophoresis

Electroosmosis and elecgrophoresis phenomena can be utilized for the solution of a number of practical problems, the solving of which by other means is difficult because of factors involved in the construction and utilization of the necessary equipment.

Such problems comprise for example, dehydration of colloidal substances which are difficult to filter; separation of colloids from extraneous impurities, for instance purification of glue, gelatin, solutions of introcellulose; separation of aqueous oil emulsions, fractionation of colloidal suspensions, precipitation of rubber from latex, impregnation of fabrics, tanning of leather, purification of glycerol, fruit juices, purification of water, and so forth.

Utilization of electroosmosis and electrophoresis with attainment of efficacy in practice is possible only in the case of liquids having a very low specific electrical conductivity. This follows not only from the velocity equations of electroosmosis and electrophoresis but also from consideration of the fact that in liquids having higher electrical conductivity, due to the presence of electrolytes concurrently with electroosmosis or electrophoresis there will take place electrolysis, which will result in extensive losses of current and excessive uneconomical expenditure of power.

Another limitation of a strictly technological nature is the difficulty of selecting rigid diaphragms which acquire a positive charge in aqueous solutions. Utilization of non-rigid diaphragms made of vegetable fibers is frequently connected with disadvantages due to their low mechanical durability.

For a successful technological utilization of electroosmosis and electrophoresis it is of great importance to have a large drop of electrokinetic potential. To attain this the suitable electrolytes are added in strictly controlled concentrations. Increased drops of potential or negatively charged diaphragms or particles can be attained by introduction of small amounts of alkali.

B. Industrial Utilization of Electrokinetic Processes

1. Dehydration of Peat

Freshly recovered peat contains water in amounts reaching 90 percent. Water is retained in peat due to the colloidal nature of humic acids present therein. Removal of water by filtration is most difficult, since the colloidal peat particles rapidly obstruct the pores of the filter; consequently induced dehydration of peat is costly. Hence peat is subjected to spontaneous dehydration in stacks by the action of wind and solar heat. Usually peat is dried to a water content of 25-30 percent.

The phenomenon of electroosmosis can be used for peat dehydration. On contact with water, the peat particles become charged negatively, while the water acquires a positive charge. Drop of the electrokinetic potential increases on addition of small amounts of alkali. On passage of an electric current through the peat slurry, the colloidal peat particles move toward the anode, and the water to the cathode ~~wherefrom~~ which it is continuously removed.

For the electroosmotic drying of peat there has been constructed a special electroosmotic filter press, in which the peat is subjected simultaneously to pressure and action of an electrical field.

Figure 66 shows the diagram of two plates of an electroosmotic filter press. Each plate consists of a rectangular iron frame, 2 - rubberized for electric insulation. One side of each frame is covered with filter cloth - 3, which is in close contact

with a perforated iron cathode - 4. The other side of the frame is in contact with a massive anode - 1, made from hard lead. The filter press can consist of any number of individual plates, which are assembled into a unit held by a compression mechanism. Anodes and cathodes are disposed alternatively between the plates. All the cathodes and anodes are connected in parallel to a circuit of direct current. The voltage is maintained at about 70 volts.

Figure 66. Diagram of electroosmotic filter press chambers 1 - anode; 2 - frames; 3 - filter cloth; 4 - perforated cathode.

Natural peat containing about 90 percent of water is ground to a slurry and charged to the filter press. Dehydration is effected at a temperature of about 45 degrees. On passage of the current, the colloidal peat particles are deposited as a thick layer on the lead anode, while the water passes through the cloth and flows down the cathodes.

Practice has shown that by means of electroosmosis it is possible to decrease the water content only to 65 percent, since most of the water in peat is present in adsorbed state, whereas the electrokinetic method removes only the mechanically held water. Power expenditure per 1 ton of peat containing 65 percent of water amounts to about 130 kilowatt hours.

The peat removed from the electroosmotic filter press cannot be directly used as fuel and requires further drying. The low cost of peat fuel and the necessity of additional drying make difficult a wide utilization of this method by the industry.

2. Purification of Kaolin

Considerably more successful is the utilization of electrophoresis in the dehydration and purification of kaolin from such admixtures as for example iron compounds, sand, pyrite and the like, which are detrimental in subsequent processing of kaolin. The suspension of clay in water is charged negatively. To increase the electrokinetic potential and the stability of the suspension, a weak alkali is added, for instance water glass, ammonia and humic substances. Coarse particles of admixtures are removed by sedimentation of the suspension, after which further purification and dehydration are effected by electrophoresis. For this purpose there is used either the electroosmotic filter press, similar to that previously described, or an osmosis machine.

Figure 67 shows the general view of an electroosmotic filter press used for clays and kaolin. The clay suspension is continuously fed into the filter press plates which, in contradistinction with those of the peat filter press, are equipped with filter cloth on the anode side as well as on the cathode side. On switching on of the current, the colloidal clay particles are deposited on the anodic cloth and the water flows off the cathode. The material is fed to the press until a solid filter cake is formed on the anode. The filter press is then opened and the deposit of pure kaolin is removed from the anode. Water content of the dehydrated cake reaches ~18 percent for clays, and ~35 percent for kaolin. Expenditure of power per ton of kaolin is from 12 to 20 kilowatt-hours.

Figure 67. Overall view of electroosmotic filter press.

A diagram of a device of a different type, the osmosis machine, is shown in figure 68. Operation of the osmosis machine is based exclusively on electrophoresis; the osmosis machine is not provided with any filter cloth. Design and operation of the osmosis machine are essentially as follows: In an oblong trough 1, there is fixedly installed a reticulated cathode 2. As the anode there is used a revolving lead drum 3. The clay suspension is continuously pumped through pipe 4 into the lower portion of the trough where it is maintained in dispersed condition by means of rotating propeller agitators 5. Through the apertures in the cathode the suspension reaches the anode, upon which the clay particles are deposited forming a layer having a thickness from 3 to 6 millimeters. The clay is being continuously removed from the anode by the doctor blade 6. The water freed of clay flows out of the trough through channel 7 and is used in the preparation of new batches of suspension.

Figure 68. Diagram of osmosis machine for kaolin purification
1 - trough; 2 - screen electrode; 3 - rotating drum (anode);
4 - pipe; 5 - propeller mixers; 6 - blade; 7 - channel.

Voltage is maintained at the 75 to 100 level with a current density at the anode of about 0.01 ampere/centimeter square. Power expenditure is of 25 to 40 kilowatt-hours per 1 ton of kaolin having a moisture content of 35 percent.

Kaolin and clay purified by electrophoresis are utilized in large quantities in the production of ceramics and in the chemical and pharmaceutical industries.

3. Purification of Glue and Gelatin

In order to purify glue from admixtures (electrolytes, proteins, colored pigments) there can be made use of a combined electrolysis and electrophoresic procedure.

The glue is first freed of electrolytes. To do so an electrolysis is first conducted in apparatus A (figure 69). The heated glue is placed into the middle compartment 1, enclosed between two diaphragms 2.

Figure 69. Diagram of apparatus for glue purification
A - apparatus for preliminary purification of glue from electrolytes: 1 - middle compartment; 2 - diaphragm; 3 - cathode compartment; 4 - anode compartment

B - Apparatus for subsequent glue purification from other admixtures: 1 and 4 - middle compartment; 2 and 5 diaphragms; 3 - anode compartment; 6 - cathode compartment.

The size of foramina of the diaphragms is selected in such a manner, that they allow the passage of only ions. The cathode space 3 and that of the anode 4 are filled with water. When the current is switched on, at 15 to 20 volts, the electrolysis process takes place as a result of which the ions move from the middle

compartment to the corresponding electrodes. As the ions are removed from compartment 1, resistance of the glue increases and the voltage is raised to 70-100 volts.

Thereafter the glue freed of electrolytes is placed into the apparatus B (figure 69), which has an additional diaphragm 5, which allows the passage of glue particles and retains other admixtures. Sections 3, 4 and 6 are filled with water. At a voltage of about 110 volts the glue moves toward the cathode and enters Section 4. On evaporation pure glue is obtained. Power expenditure per 1 kilogram of glue is of about 8-9 kilowatt-hours. Other colloids are purified by an analogous method.

4. Precipitation of Rubber

Natural rubber is obtained from the milky juice (latex) of rubber-bearing plants. The rubber is present in the milky juice in the form of an emulsion. In the latex the rubber is charged negatively and on electrophoresis is deposited on the anode. Electrophoretic separation of crude rubber from the latex is used in rubber manufacturing practice. However, electrolytes present in the latex impede this process primarily because concurrently with electrophoresis, electrolysis takes place. As a result of this, gases are liberated at the anode which inhibit uniform precipitation of rubber and in addition render the deposit friable. To avoid these complications a number of expedients is used, for instance the electrophoresis is conducted with a low anodic potential, which inhibits discharge of ions, soluble metals are used as the anode, reducing agents are added to the cell, and finally the

anode is surrounded by a non-conducting diaphragm made of parchment or asbestos upon which the rubber is deposited.

In the precipitation of rubber, there are used either osmosis machines or a specially designed apparatus comprising an endless belt, which is shown diagrammatically in figure 70. In the trough 1, filled with latex, an endless band travels upon rollers made of wire mesh which constitutes the anode. At the bottom of the trough the cathode 2 is located. Rubber is deposited on the band-anode and is carried with it under the water jet nozzles 3, which effect its washing. The band then travels over a drying Table 4, and the dried rubber layer is removed by blade 5.

The rubber can be deposited together with additives necessary for vulcanization and coloration if these additives are also negatively chargeable colloids. In such a case, the additions are made into the emulsion in finely divided form.

Figure 70. Diagram of apparatus for rubber precipitation. 1 - trough; 2 - cathode; 3 - water nozzles; 4 - drying table; 5 - blade.

Electrophoretic precipitation of rubber together with additives is also used in the production of rubberized fabrics, of rubber coated metallic instrument parts having involute surfaces, of iron grates and the like.

Figure 71 shows the diagram of an apparatus for the production, by the continuous method, of rubber impregnated fabric. The band of fabric 1, travels over rollers, passing along the anode 2.

The anode is made of perforated sheet metal and is provided at its back side with a box connected to the vacuum tube 4. This device makes it possible to avoid swelling and porosity of the rubber deposit on the fabric, since gases liberated on the anode are continuously removed through the tube 4.

Figure 71. Diagram of apparatus for production of rubberized fabric:
1 - band of fabric; 2 - anode; 3 - box; 4 - vacuum tube.

5. Tanning of Leather

Old methods of leather tanning require the expenditure of a great deal of time. Depending upon the grade and the thickness of the leather, the tanning process proceeds over a period of many months.

Among the various methods of speeding up the tanning process, the electrophoretic method is one of great importance.

The tanning process consists in a penetration of the tanning agent into the substance of the hide and the reaction with that substance. Penetration of the tanning agent can be accelerated by means of electrophoresis. The hide being tanned plays the part of a positive diaphragm in this case through which flows the tanning substance which constitutes a negatively charged colloid. Under the action of the electric field, the speed of penetration of the tanning agent is considerably increased and duration of tanning is correspondingly reduced to a few days.

Electrophoretic tanning is conducted in large wooden vats. The vats are filled with tanning liquor and several scores of skins are immersed in them, the skins being suspended in parallel alignment. At opposite ends of the vats, hard lead electrodes are placed parallel to the suspended skins.

To guard against oxidation of the tanning agent at the anode, and its reduction at the cathode, the electrodes are contained in canvas bags, or in wooden boxes one side of which is covered with canvas. A stream of water is made to flow through the canvas bags or wooden boxes so as to remove from the electrode space the electrolytes which permeate thereto from the tanning liquor in which these electrolytes are always present.

According to the technique of skin processing, tanning is effected consecutively in several vats containing increasing concentrations of tanning agent. In this process the voltage varies from 80 to 150 volts and the current from 100 to 150 amperes.

6. Electroosmotic Purification of Water

River or ground water always contains a certain amount of mineral admixtures -- various soluble salts and suspended colloidal particles. Water containing large amounts of admixtures is often unsuitable for use and hence must be purified. Water purification methods are most varied and are selected depending upon the nature of the admixtures and the requirements of the use to which the water is to be put.

For the purification of water, various chemical methods and distillation are used. Chemical methods are based on elimination

of the soluble admixtures in the form of little soluble compounds. A complete purification is not attained thereby, but admixtures consisting of detrimental salts are replaced by other less detrimental ones. In cases when complete elimination of admixtures is acquired, the water is distilled once or twice. To save steam, the distillation is conducted in multiple-unit evaporation devices.

The need for very pure water, free from salt admixtures, is very great. Such a water is used, for example, as feed in high pressure steam boilers, in the production of storage batteries, in the pharmaceutical and chemical industries, for use in laboratories and so forth.

In many instances when very pure water is needed, it is found to be convenient in practice and economically advantageous to effect purification of the water by a combined electrolytic-electroosmotic method. By this method it is possible to purify very impure water containing several hundred milligrams of dry residue per liter, and to obtain water that is practically free of salt admixtures, the content of which in the purified water can be reduced to tenths of a milligram per liter.

Equipment for electroosmotic purification of water is very simple in design and requires almost no operating personnel. The main operational expense is the expenditure of electric power, which varies depending on the amount of impurities present in the water and the degree of purification attained. In the purification of water to a content of 5-7 milligrams of dry residue per liter, the power expenditure per one cubic meter of purified water can be

computed by using the following empirical formula:

$$w = 0.0025\ gE \text{ Kilowatt-hours} \qquad (4)$$

wherein g is the final content of dry residue in milligrams per liter, and E the average voltage per cell of the apparatus.

The general principle of electroosmotic water purification method is the same as that of electrolytes removal from glue. Water is fed into the apparatus which is divided into three sections by means of two diaphragms. The two end sections are the anode and cathode compartments respectively. Water flows continuously through the middle section, and the ions present in the water pass through the diaphragms into the cathode and the anode compartments.

For an electroosmotic purification of water on an industrial scale there can be utilized an apparatus, the principle of design and operational diagram of which, are shown in figure 72. The apparatus consists of individual electroosmosis cells I, II, III . . . X (usually ten cells). Each cell is divided by means of diaphragms 1, into three sections; 2 - the anode compartment, 3 - middle compartment and 4 - cathode compartment. The end compartments contain the corresponding electrodes. Water from tank 5 flows into all three sections of the first cell, and also into the cathode and anode compartments of cells two to nine inclusive.

Figure 72. Diagram of electroosmotic installation for purification of water: 1 - diaphragms; 2 - anode compartment; 3 - middle compartment; 4 - cathode compartment; 5 - water tank; 6 and 7 - pipes; 8 - pure water tank.

In the first cells only an electrolysis process takes place as a result of which the ions migrate from the middle compartment into the end compartments. Thus the water in the anode compartments becomes acidic while in the cathode compartments it becomes alkaline. The acidic and the alkaline water are discharged from the electrode compartments through pipes 6 and 7. From the middle compartment of the first cell the water flows through a syphon into the second and so on, consecutively passing through all ten cells.

In the tenth cell the water undergoes final purification from electrolytes and colloidal admixtures and is then pumped into the pure water tank 8. As the water passes from the first to the last cell its purity increases, and its conductivity decreases, and consequently the resistance of the cells becomes greater. Therefore the cells are connected to the electrical circuit in such a manner that the voltage in them increases gradually. Usually the ten cells are divided into four groups, the first consisting of four cells, the second of three, the third of two and the fourth of one cell. All four groups are connected to the circuit in parallel, while the cells of each group are connected in series. The direct current voltage used is usually within the limits of 110 to 220 volts. At 220 volts, each cell of the first group operates at 55 volts, those of the second group at about 73 volts, those of the third at 110 volts, and the tenth cell at the voltage of the circuit -- 220 volts.

The degree of water purification is materially affected by the concentration of acid and alkali in the electrode compartments. On excessive increase of the concentration of acid and alkali the

purification effect is lessened, since alkali and acid penetrate into the middle compartment to the detriment of diffusion and electrotransfer of ions.

In order to maintain the concentration of acid and alkali at a definite level, the electrode compartments are flushed continuously. In the first cells untreated water is used for flushing, the intermediate cells are flushed with partially purified water, and the last, the tenth cell, is flushed with fully purified water. Acidic, anode water are discarded to the sewer; alkaline, cathode water can be utilized for flushing as well as fed into the middle compartments.

The apparatus described is embodied in practice not in the form of a number of individual cells but as a unit assembly of the filter press type (figure 73).

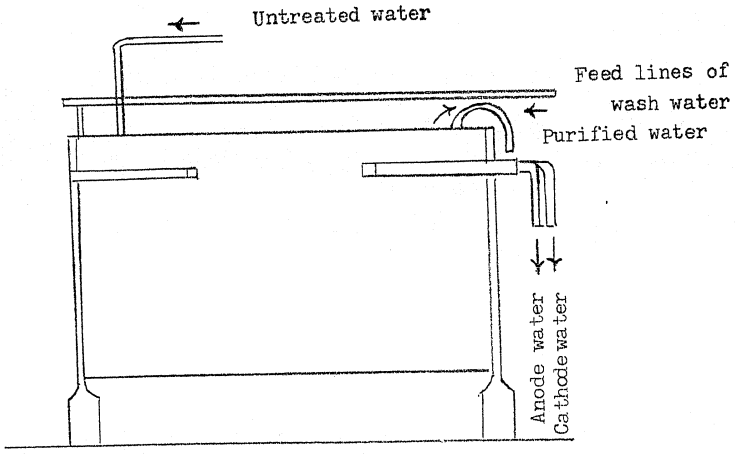

Figure 73. Diagram of filter press electroosmotic apparatus for purification of water.

Each cell consists of three U-shaped iron frames. The middle frame is rubber coated and is provided on each side with a diaphragm. Each cell is separated from the adjoining by a sheet of ebonite, and the entire unit is held together by means of iron clamping bars which are threaded and provided with hand wheels. Anodes are made of magnetite, graphite or lead; the cathodes of magnetite, zinc or iron.

To facilitate the passage of ions through the diaphragms, material for making them is selected so that the anode diaphragm acquires a positive charge, and the cathode diaphragm a negative charge. In water a negative charge is acquired mostly by materials of vegetal origin, while those of animal origin are charged positively.

Accordingly cathodic diaphragms are made of cotton fabric, and the anodic diaphragms of chrome gelatin; the latter are produced by impregnating a fabric with a 10-20 percent solution of gelatin to which has been added from 3 to 6 grains of bichromate for every 100 milliliters of the solution. The impregnated fabric is subjected to intensive illumination for a period of several hours; the chrome gelatin is thus made insoluble.

It is of great importance that the anodic diaphragms be stable toward the acidic anolyte, and since chrome gelatin is not entirely satisfactory in this respect, there are used diaphragms made of vulcanized fiber material, porous ebonite and ceramic material. Inasmuch as the sign of the diaphragm charge is not determinant in some instances, both diaphragms are made of cotton. Glass tubing is used to make the syphons.

The equipment is made to have an output of 4, 20, 80 and 180 liters of purified water per hour, on using untreated water containing 300 milligrams of dry residue per liter, and yields water wherein this content is reduced to 8-10 milligrams per liter.

Dimensions of a unit of 180 liters per hour capacity are: length 2500 millimeters, width 2000 millimeters, height 1500 millimeters. Floor space required by the cells, to give one cubic meter of water per hour, is of about 22.5 square meters.

Power expenditure and output of the device, as was stated previously, depend upon the quality of the untreated water and that of the purified water.

One cubic meter of purified water requires 15 kilowatt-hours if the untreated water contains from 100 to 150 milligrams per liter of dry residue, and this amount is reduced to 8-10 milligrams per liter in the purified water.

Apparatus for the purification of water have been considerably improved in recent times.

Figure 74 shows a cylindrical electroosmosis cell. It consists of a cylindrical iron casing 1, 250 millimeters in diameter, about 1000 millimeters high with a removable iron bottom and an ebonite cover. Inside the iron cylinder is a cylindrical anode diaphragm 2, made of porous ceramic material, which is 150 millimeters in diameter and has a wall thickness of about 7-8 millimeters. It is fitted on the outside with ebonite rings 3, onto which is wrapped the cathode diaphragm 4 made of asbestos fabric.

Thus the cell is divided into three compartments: central (anodic), middle, and outer (cathodic). The width of the cathode compartment and that of the middle, ring-containing compartment, is of about 20 millimeters. The wall of the iron cylinder serves as the cathode, which is connected to the negative terminal of the source of current. The anode is formed by platinum wires 5, fastened to the ebonite cover of the cell, and extending inside the ceramic cylinder.

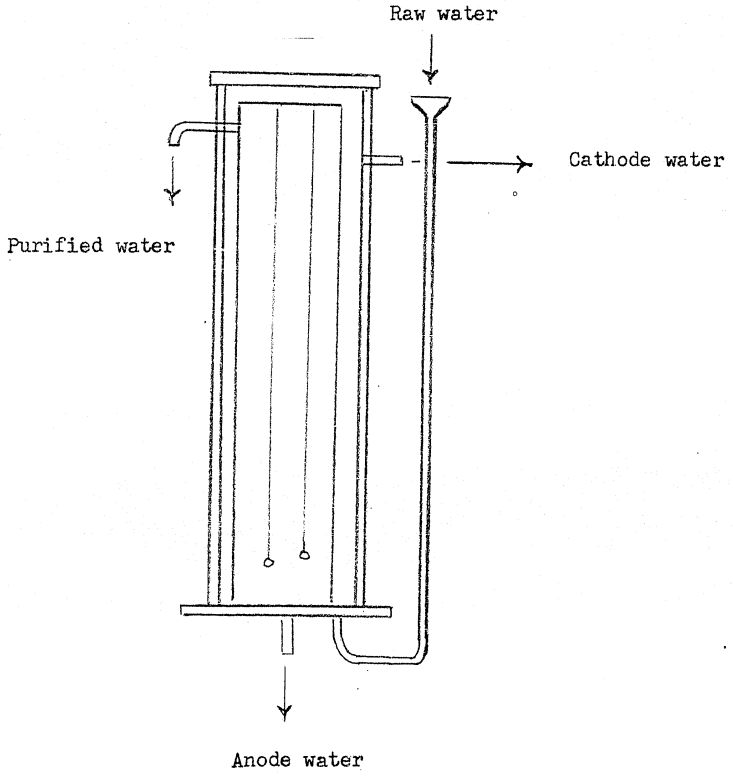

Figure 74. Diagram of cylindrical electroosmotic cell. 1 - iron casing; 2 - anodic diaphragm; 3 - ebonite rings; 4 - cathodic diaphragm; 5 - platinum wires; 6 - transfer pipe.

Water to be purified enters at the bottom into the middle compartment. Rising upwards it undergoes purification and flows out of the overflow pipe 6. The water level in the middle compartment is maintained 15-20 millimeters above that in the cathode compartment, as a result of which about 10 percent of the water from the middle compartment percolates into the cathode compartment thus creating a counter-current which inhibits diffusion and electrotransfer of alkali from the cathode compartment into the middle compartment. The water does not flow through the anode compartment, but periodically a portion of it is let out through the bottom pipe at such a rate that the acidity is maintained at about 5 percent. The cathode compartment is occasionally flushed to remove the sediments.

Design and operation of the described devices are very simple. The devices can be manufactured in different output capacities and several of them connected in series.

Figure 75 shows the diagram of an installation yielding 200 liters of purified water per hour and consisting of four consecutively connected cells of the above-given dimensions. The unit operates at 15 amperes with a voltage of 220 volts.

Untreated water containing about 150 milligrams of dry residue per liter, flows from a pressure tank into the first cell from which it flows through a pipe into the middle compartment of the second cell. On passing successively through all the cells, the water leaves the fourth cell purified to a content of 5-7 milligrams of dry residue per liter, which corresponds to a specific resistance of about 70 000 ohms.

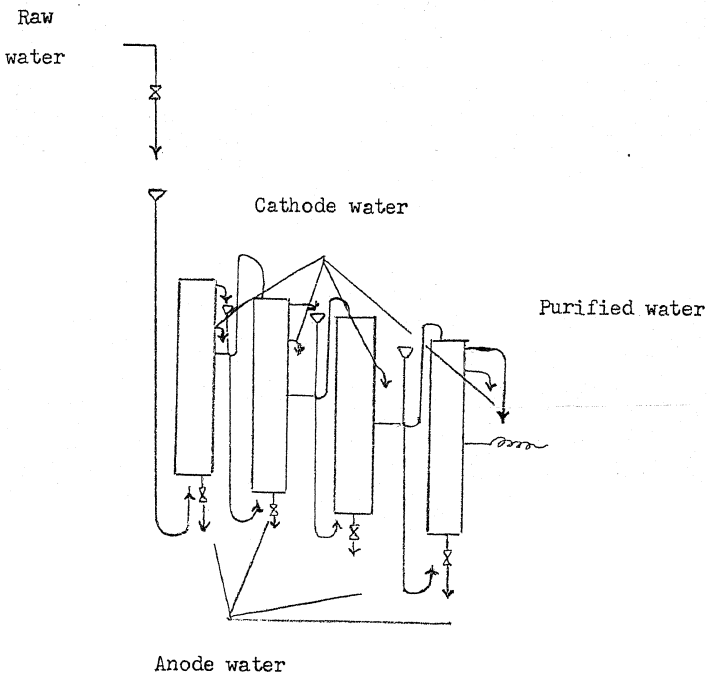

Figure 75. Diagram of installation of cylindrical electro-osmotic cells.

Power expenditure per cubic meter of purified water is given in Table 19.

Table 19

Power expenditure in Kilowatt-hours, per cubic meter of purified water

Voltage in volts	Dry residue content of untreated water milligrams/liter		
	100	200	300
110	6	12	18
220	12	24	36

Further increase of volumetric output has been attained in the cell of Soviet design shown in figure 76.

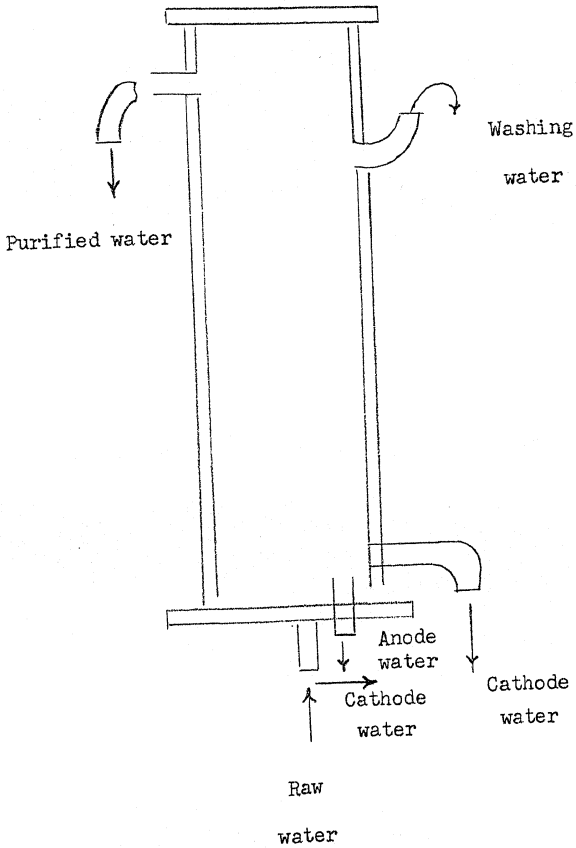

Figure 76. Electroosmotic cell of Soviet design. 1 - supplementary cathodic iron cylinder; 2 - Apertures for discharge of cathode water; 3 - outlet pipe for discharge of cathode water; 4 - cathode diaphragms; 5 - anode diaphragm; 6 - platinum anode; 7 - inlet pipe for raw water; 8 - transfer pipe for discharge of purified water; 9 - pipe for discharge of wash water; 10 - pipe for removal of cathode water; 11 - pipe for removal of anode water.

The outside casing of the cell made of iron is 220 millimeters in diameter, 1000 millimeter high and has an iron bottom and ebonite cover.

Inside this external cylinder which serves as the cathode, there is a second iron cylinder cathode 1, having a diameter of 76 millimeters, provided at the top and bottom with apertures 2 for the egress of cathodic water by way of outlet pipe 3. Around the cylinders, on ebonite spacer rings, there are located concentrically, two cathode diaphragms 4 made of asbestos fabric. The cell is thus divided into three annular compartments (20 millimeters wide): outer and center cathode compartments, and a middle, inter-diaphragm compartment. In the middle compartment there are located ten tubular anode diaphragms 5, 20 millimeters in diameter made of porous ceramic material. Inside the anode diaphragms are the anodes 6 consisting of platinum wires attached to the ebonite cover. Untreated water is fed into the middle (interdiaphragm) compartment at the bottom through pipe 7, and on rising upwards, flows out through overflow pipe 8. Cathodic water is withdrawn from the outer cathode compartment through pipe 10, and from the inner cathode compartment through pipe 3. In flushing the cathode compartment to remove sediments, the liquid is let out through pipe 9. Anodic water is periodically let out through pipe 11.

Two such cells connected in series yield 200 liters of purified water per hour, when the untreated water contains 250 milligrams of dry residue per liter, and the purified 5 milligrams per liter. The cells operate at 25 to 35 amperes intensity with a

voltage of 120 to 220 volts. Power expenditure amounts to about 31 kilowatt-hours per one cubic meter of water.

Improvement of electroosmosis apparatus for the purification of water opens wide prospects for their utilization in practice. Being of simple design they do not require constant supervision and servicing like distillation units. Especially advantageous and convenient is their use in the purification of small amounts of water, when power expenditure is not the deciding factor in comparison with dependability and simplicity of operation.

CHAPTER V

ELECTROLYTIC PRODUCTION OF HYDROGEN AND OXYGEN

The simplest method of obtaining hydrogen and oxygen in a pure state is the electrolysis of water. If cheap hydroelectric power is available, electrolysis of water is also economically the most advantageous method of manufacturing hydrogen and oxygen.

Modern industry requires large amounts of hydrogen and oxygen. Though only 30-40 years ago hydrogen had practically no value as an industrial raw material. The use of hydrogen was limited to utilization of very small amounts, mainly in aeronautics, lead burning, fat hydrogenation and for illumination. These requirements were met to a considerable extent by use of hydrogen obtained as a by-product in the electrolytic production of chlorine and caustic. Consequently, development and improvement of various methods of hydrogene production, among them by means of water electrolysis, were of no great significance. Industrial value of hydrogen has increased abruptly with the initiation and development of synthetic ammonia production, which required large amounts of pure hydrogen.

Significance of electrolytic hydrogen production is determined by increased industrial utilization of hydrogen and by the advantages inherent in this method for its production (simplicity of operation, purity of the gases, and with availability of cheap electric power the possibility of competing economically with the other methods, especially under conditions permitting utilization of the oxygen).

At the present time, electrolytic production of hydrogen and oxygen is one of the important branches of electrochemical industry. Large installations for electrolytic production of hydrogen and oxygen are available in all industrial countries. But their greatest development has been attained in countries having large resources of hydroelectric power and limited sources of fuel.

Alongside with large scale installations producing up to 20 thousand cubic meters of hydrogen per hour, there are operating in the industry numerous small units, producing each several hundred cubic meters of hydrogen per 24 hours. Small installations are being built for hydrogenation of fats, for metal cutting and welding, for lead burning, production of incandescent lamps, storage batteries, artificial precious stones and the like. Production of hydrogen by water electrolysis is especially advantageous in those cases when there is also a use for the oxygen such as for instance for metal cutting and welding, lead burning and so forth.

In the USSR there existed previously only small installations for electrolytic production of hydrogen and oxygen. In recent years a large amount of research and designing work has been conducted as a result of which cells of new types have been developed for use in large and small installations.

At the present time in the USSR there are large installations for the electrolytic production of hydrogen and oxygen.

Hydrogen and oxygen were first obtained by decomposition of water with an electric current in 1789. However, for over 100

years this process had no practical utilization and was limited to laboratory demonstrations.

In 1888 a Russian scientist, professor D. A. Lachinov had built the first apparatus for producing hydrogen and oxygen electrolytically. In his patents Lachinov envisaged production of hydrogen and oxygen at ordinary as well as increased pressure and also proposed construction of cells having monopolar and bipolar electrodes.

The first industrial installations for an electrolytic production of hydrogen and oxygen made their appearance in the nineties of the last century. Naturally the output of individual cells and installations was very small. In line with the small scale production, not sufficient attention was then devoted to both efficient utilization of electric power and compactness of equipment. In the early twenties of the current century there takes place intensive research and construction activity having for its primary goal reduction of the amount of electric power consumed in the electrolysis and decrease of cell dimensions with concomitant increase of their output capacity.

In the new designs, extensive attention is devoted to improvement of the electrodes, circulation of electrolyte, reduction of gas-saturation, decreasing the distance between electrodes so as to attain maximum reduction of power expenditure and to increased output per unit of volume of the cells. Within the same period work is renewed on designing large capacity filter-press cells.

On the basis of the new improved type of cells the construction of large installations for electrolytic hydrogen production in conjunction with synthetic ammonia and fat hydrogenation plants has been begun.

Simultaneously with improvement of cells operating at ordinary pressure, renewed interest is manifested in water electrolysis under increased pressure.

A. Theoretical Basis of Electrolytic Production of Hydrogen and Oxygen

1. Properties of Hydrogen and Oxygen

Of the physical constants of hydrogen and oxygen we shall note those which must be taken into consideration in rating of equipment and manufacturing operations (Table 20)

[See next page for Table 20]

Within the range of -190 degrees to +100 degrees the heat conductivity can be calculated using the formula:

$$\lambda = \lambda \frac{(273 + c)}{T + c} \left(\frac{T}{273}\right)^{3/2}$$

wherein: λ - heat conductivity at 0 degrees, equal to 0.136 for hydrogen and 0.02 for oxygen.

c - coefficient equal to 94 for hydrogen and 144 for oxygen.

T - absolute temperature.

Table 20

Physical Constants of Hydrogen and Oxygen

Constants	Hydrogen	Oxygen
Molecular weight	2.016	32.000
Density at 0° and 760 mm pressure; gram/liter	0.08987	1.4289
Volume of gram-mole; liter	22.433	22.393
Density relative to air	0.06952	1.1053
Van der Waal's equation constants per mole	a = 0.19 b = 0.023	a = 1.36 b = 0.0316
Gas constant liter atmosphere/kilogram degree	42	2.65
Viscosity at 0°; poise	8.5×10^{-5}	1.915×10^{-4}
Boiling point; °C	-252.7	-183
Critical temperature; °C	-239.9	-118.8
Crystallization temperature; °C	-259.1	-218.8
Critical pressure; atmosphere	12.8	49.7
Critical density; gram/cm^3	0.031	0.430
Heat capacity, molar (C_p	$6.5 + 0.0009T$	$6.5 + 0.0010T$
Heat capacity, molar (C_v	$4.52 + 0.0009T$	$4.52 + 0.0010T$